Kawasaki dynamics and equilibrium distributions in simulations of phase separating systems

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Abstract

We compare equilibrium probability distributions obtained from Monte Carlo simulations for different spin exchange dynamics with the exact Boltzmann distribution for the fixed magnetization Ising model on small lattices. We present simple arguments and numerical evidence in order to show that "efficient" Kawasaki exchange does not lead to Boltzmann equilibrium distributions and that nearest-neighbour equal spin-exchange must be considered. Arbitrary distance opposite spin interchange is indicated as an alternative to obtaining the full phase diagram with phase separation.

Key words: Kawasaki exchange; Monte Carlo; 2d lattice gas; 2d Ising model; phase separation

Equilibrium properties under phase separation are a problem of current interest, both in simple[1] and complex solutions, such as polymer mixtures[2], microemulsions[3] or different types of solutions of amphiphile molecules in water which present liquid crystal phases or local structure such as micelles, vesicles and membranes[4]. Coexistence in simple solutions is analogous to the problem of liquid - gas coexistence and obtaining full concentration-temperature phase diagrams is still a subject of discussion in the literature[5]. As to complex solutions, even very simple lattice model systems which include finite multi-site molecules[2][6] have no analytical solution beyond Flory mean-field[7] and simulations have been one of the main tools of investigation[8]. In solutions of amphiphilic molecules or copolymers one is not only interested in describing the thermodynamic phase diagram, but one also wishes to obtain the morphology of the different phases or microphases. In fact, one is often not sure whether different morphologies represent different phases. For this reason, simulations are most often carried out at constant concentration, that is, in the canonical, rather than in the grand- canonical ensemble[9]. To obtain the equilibrium structures one must deal with the long time relaxation problem of nucleation and growth, an object of innumerous studies in the case of simple liquids[10]. We therefore found it adequate to explore the limitations of constant-density simulations[11] in relation to equilibrium properties in the critical and phase separating region. In order to be able to compare simulation and analytical results, although our interest lies in complex solutions, we chose to study the case of the Ising model at constant magnetization (or, equivalently, the lattice gas model at constant density), which corresponds to fixed relative concentrations of a model mixture of molecules of the same size. This model has been studied often enough

1

in order to obtain growth behaviour[10] and, more recently, critical dynamic exponents[12], but we found very little reference to recent studies of its equilibrium properties[15]. In order to be able to compare with analytical results, we focus attention on the two-dimensional case and equal relative concentrations, the equivalent of the magnetic model at zero field . The well-known Kawasaki spin exchange model[14], originally formulated as a kinetic model associated to a master equation, is the appropriate tool for the case. To our surprise, we found out that a straight-forward application of the spin-exchange algorithm in the form suggested by the main text-books on simulations[15] results in non-Boltzmann equilibrium distributions. The necessary search for efficiency in simulations of the spin exchange dynamics, has lead, among others[16], to the idea of selecting opposite pairs of spins in order to save computer time[17]. However, this time-saving procedure in the choice of trial exchange moves does not fulfill the detailed balance condition and therefore produces incorrect equilibrium distributions[18] , as we show below.

Kawasaki dynamics in simulations is presented in textbooks[14] as an algorithm in which one must find a pair of opposite sign nearest neighbours and try to exchange them according to some detailed balance criterion, for example, the Metropolis prescription[19]. Exchanging spins of the same sign does not alter the configuration and would apparently mean a waste of time. The difficulty in obtaining convergence of the thermodynamic properties of the model in the large L limit to the known analytic forms lead us to compare equilibrium properties of the model obtained through different procedures for the trial moves. As long as one is not interested in dynamic properties[10], the choice of kinetic model should be irrelevant. We have applied different density conserving algorithms to the zero magnetization Ising model on a square lattice. Three of them are presented in this paper: (i) interchange of nearest neighbours selected randomly among pairs of unlike spins, (ii) exchange of nearest neighbours selected randomly, independently of sign (this includes moves which do not alter the configuration of spins) and (iii) interchange of spins selected randomly among pairs of unlike spins, but independently of distance. These three procedures lead to the distribution curves for the spin configurations shown in fig 1, where the exact Boltzmann distribution is also shown, since it is easily calculated for such small lattice ($L = 4$). The striking fact is that method (i) leads to a non-Boltzmann equilibrium distribution. The reason for this result is, as a matter of fact, quite simple, as we try to illustrate below.

Consider the configuration (a) of fig 2 for an $L = 5$ lattice. According to the nearest neighbour opposite spin exchange algorithm, the probability that it turns into configuration (b) during the simulation is $\frac{1}{6}e^{-\beta \Delta E}$, because there are six pairs of opposite sign, whereas the probability that configuration (b) turns back into (a) is $\frac{1}{8}$, since there are now eight pairs of opposite sign. This does obviously not satisfy detailed balance. It is easy to think of other examples for which a bias towards higher energy configurations is present.

On the other hand, the same figs show that detailed balance will be obeyed

2

if one exchanges nearest neighbours independently of sign, or random distance pairs of opposite sign. The probabilities are, respectively, $\frac{1}{50}e^{-\beta\Delta E}$ and $\frac{1}{46}e^{-\beta\Delta E}$ for process $a \to b$ and $\frac{1}{50}$ and $\frac{1}{46}$ for $b \to a$. This explanation for our result is apparently obvious, but we found no reference whatsoever to this problem in the literature[20].

One might hope that the distortion would be smaller for larger lattices. To show that this is not the case, we compare energy distributions obtained from the different algorithms for $L = 10$ and $L = 4$ in fig 3. The Boltzmann probability distribution has not been calculated in the first case, but the comparison of the three algorithms is clear. In the case of the opposite pair exchange, the curve is slightly distorted at the edges for $L = 4$, whereas for $L = 10$ the whole curve is shifted towards higher energy values.

The effect of the distortion of the equilibrium distribution on thermodynamic quantities is quite drastic. To exemplify, we show this in relation to energy and specific heat in figs 4 and 5. Since procedures (i) and (ii) involve long relaxation and correlation times, much longer runs are needed in these cases, in relation to case (iii), as indicated in the figure captions. Fig 6 shows that proper care was taken in order to assure that these effects were taken into account. It is quite clear from figs 4 and 5, that while convergence to the expected behaviour of an infinite lattice is achieved in the case of algorithms (ii) and (iii), the first algorithm would indicate a much smaller transition temperature, as a consequence of the fact that those transition probabilities make "higher temperature configurations" more probable.

Perhaps one should recover the original formulation of Metropolis and coworkers[19], in which the transition probability is written as a product of two factors: the a priori probability which links two states a and b, which depends on the choice of movement one uses for the updates, and the exponential factor $e^{\beta(E_b - E_a)}$. For simulations in liquids, this is the usual prescription[21]. For spin systems, however, different updating procedures are of current use, with no check on the full transition probability.

We have presented results for the critical case, for clearness of argument. However, the short relaxation and correlation times presented by the random distance exchange point to the possibility of obtaining the full phase coexistence diagram from the specific heat peak [22], using finite size analysis, with small numerical cost. It thus stands as an alternative to other methods proposed in the literature[11].

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Figure Captions

Fig 1. For $L = 4$ there are 12870 spin configurations compatible with the zero magnetization thermodynamic state. The figure shows the probability distribution for the different configurations (arbitrarily numbered) at $t = 1.9$ ($t = kT/J$) according to (a) the Boltzmann distribution, (b) opposite nearest neighbour pair exchange, (c) nearest neighbour pair exchange, independently of sign and (d) opposite pair exchange at random distance. The figure illustrates the fact that opposite spin exchange (case b) does not lead to the correct distribution.

Fig 2. Two possible configurations of a fixed magnetization state for $L = 5$. If only opposite pairs are considered for exchange, transition $a \rightarrow b$ will be selected for a trial move with probability $\frac{1}{6}$, while transition $b \rightarrow a$ will be selected with probability $\frac{1}{8}$.
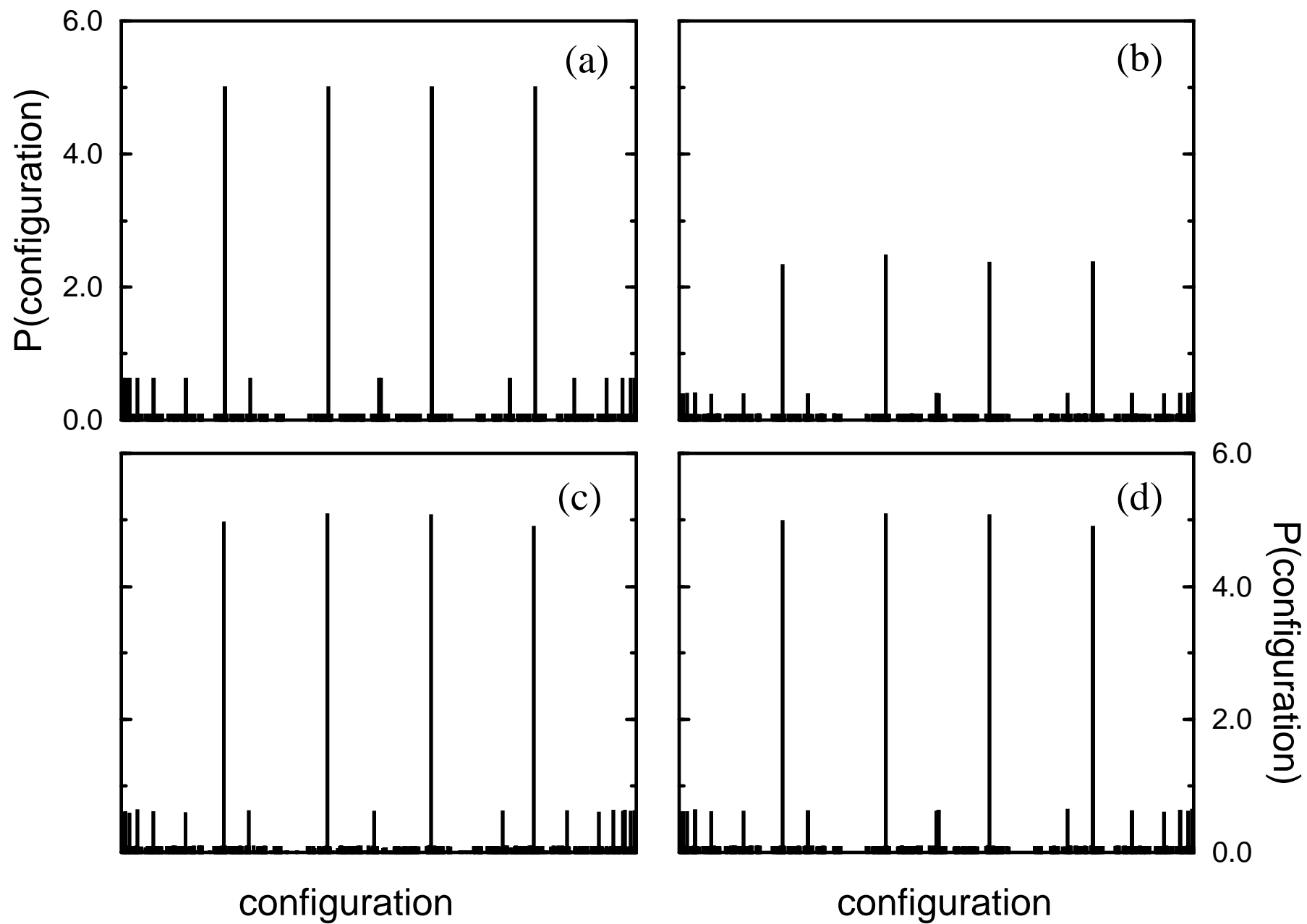
Fig 3. Energy probability distribution for (a) $L = 10$ and (b) $L = 4$ for the reduced temperature $t = 1.9$. (Δ) nn opposite pair exchange, (∇) nn pair exchange independent of sign and ($\square$) random distance opposite pair exchange results are presented in both figures. Boltzmann distribution values ($\bigcirc$) are also presented for $L = 4$ in fig (b). Typically, 10^6 MC steps were used for the nearest neighbour exchange simulations and 10^5 MC steps for the random distance algorithm.
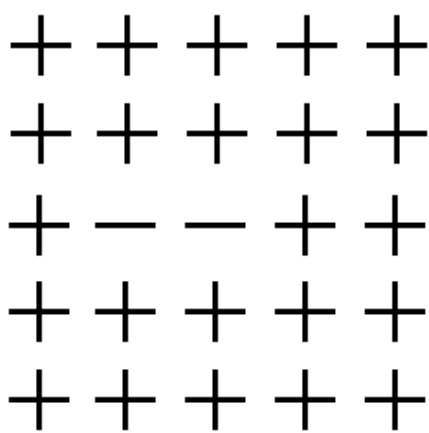
Fig 4. Energy per spin as a function of temperature for (a) $L = 80$ and (b) $L = 10$. Cases (ii) and (iii) (see text) coincide, whereas case (i) would indicate a systematically larger average energy.

Fig 5. Specific heat as a function of temperature for different lattice sizes (a) for opposite nn exchange and (b) for random distance opposite exchange. Typical runs are as in Figs 3 and 4. The exact transition temperature ($t = 2.27$) is also indicated.
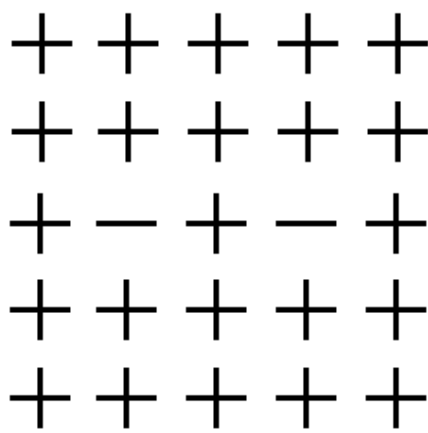
Fig 6. Energy as a function of time (in units of MC steps) for the $L = 80$ lattice (a) from the nn opposite exchange algorithm for $t = 1.95$ and (b) from the random distance algorithm for $t = 2.2$. These temperatures were chosen in the region of large fluctuations, which differ for the two algorithms. The figure shows that relaxation times (from an initial disordered microstate) are of order 15×10^4 for the first case and 5×10^3 for the random distance case. Correlation times are respectively of order 10^3 and 10 (not shown in the figure).

Figure 1

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+ + + + +          + + + + +
+ + + + +          + + + + +
+ − − + +          + − + − +
+ + + + +          + + + + +
+ + + + +          + + + + +
    (a)                (b)
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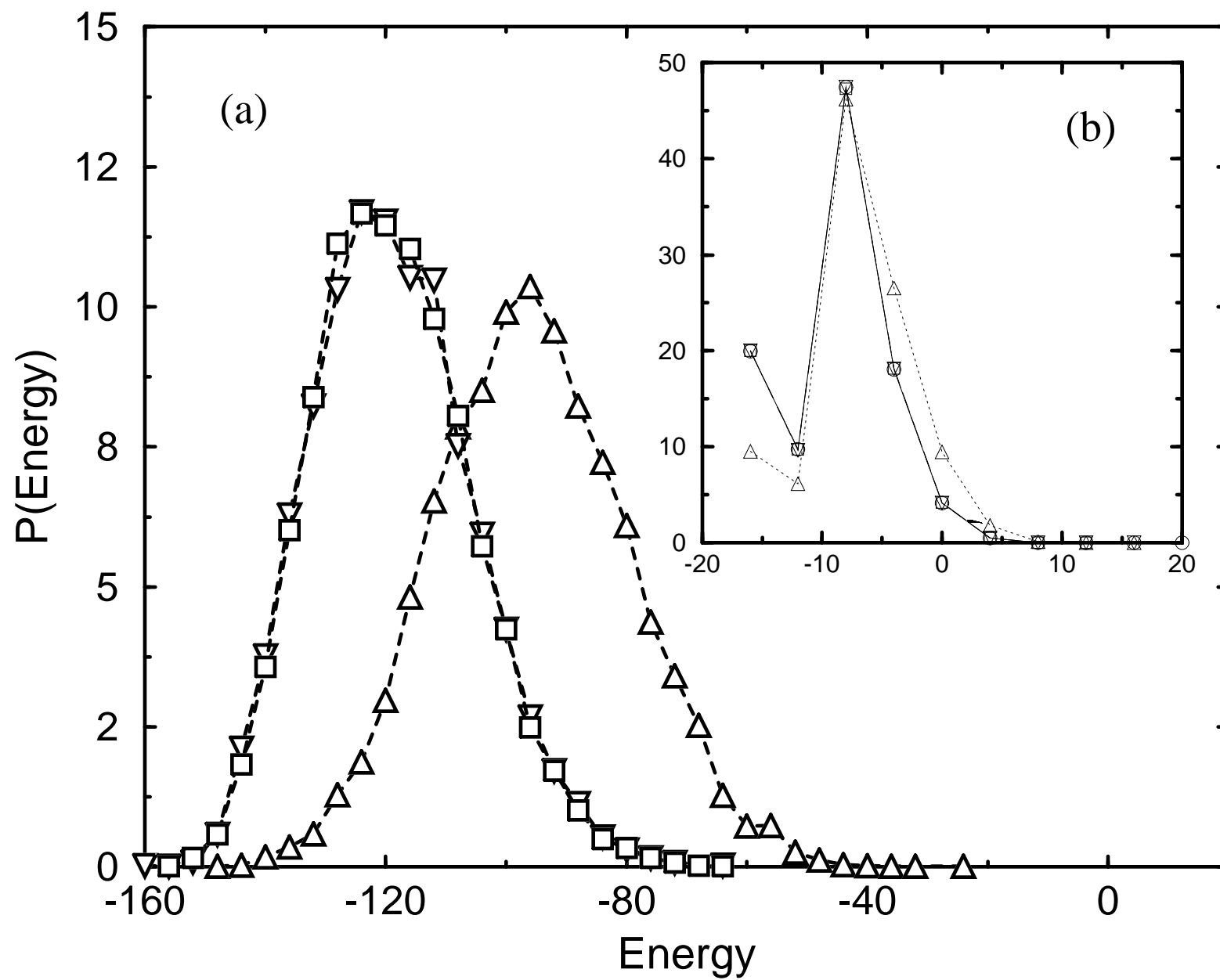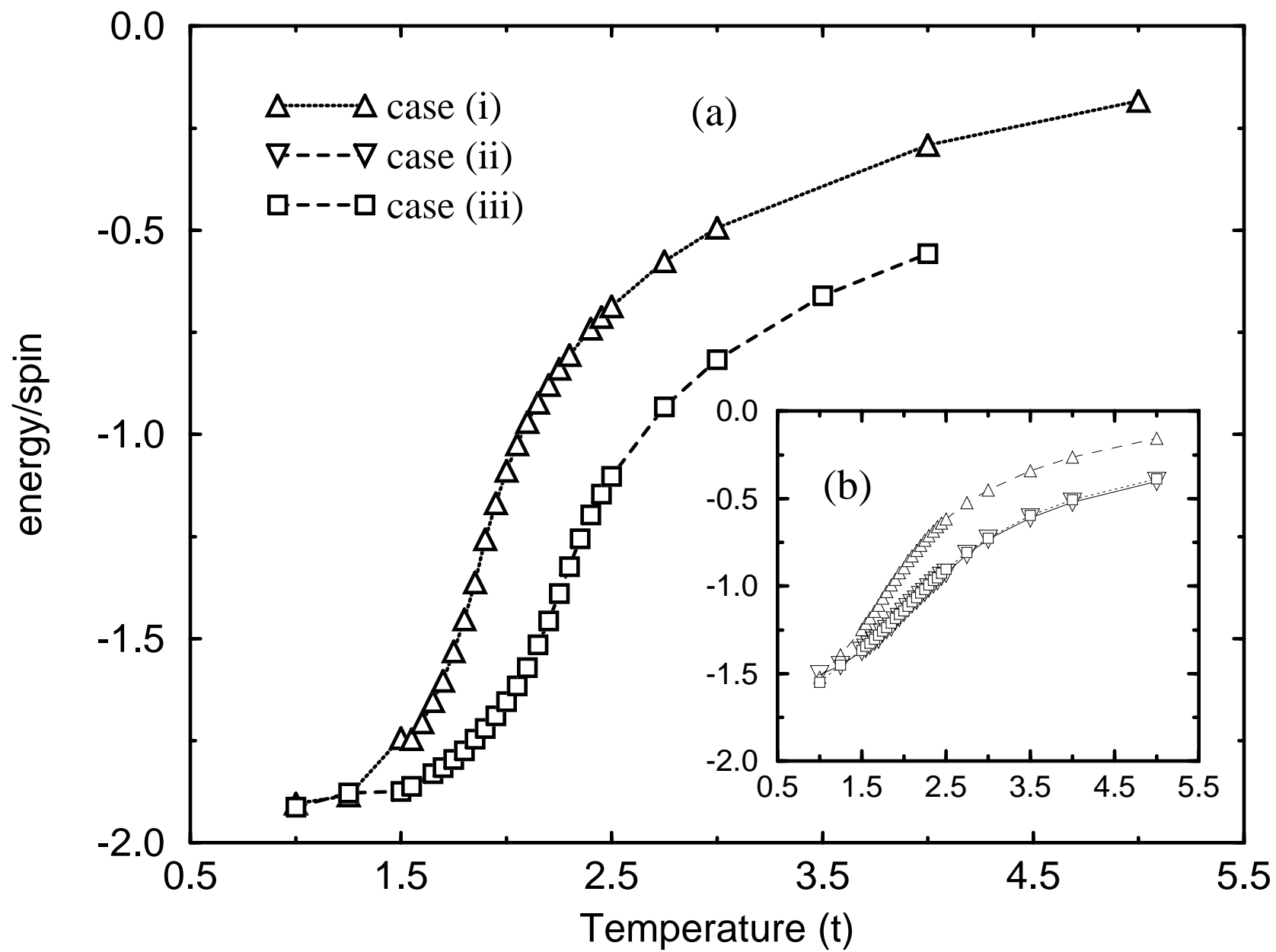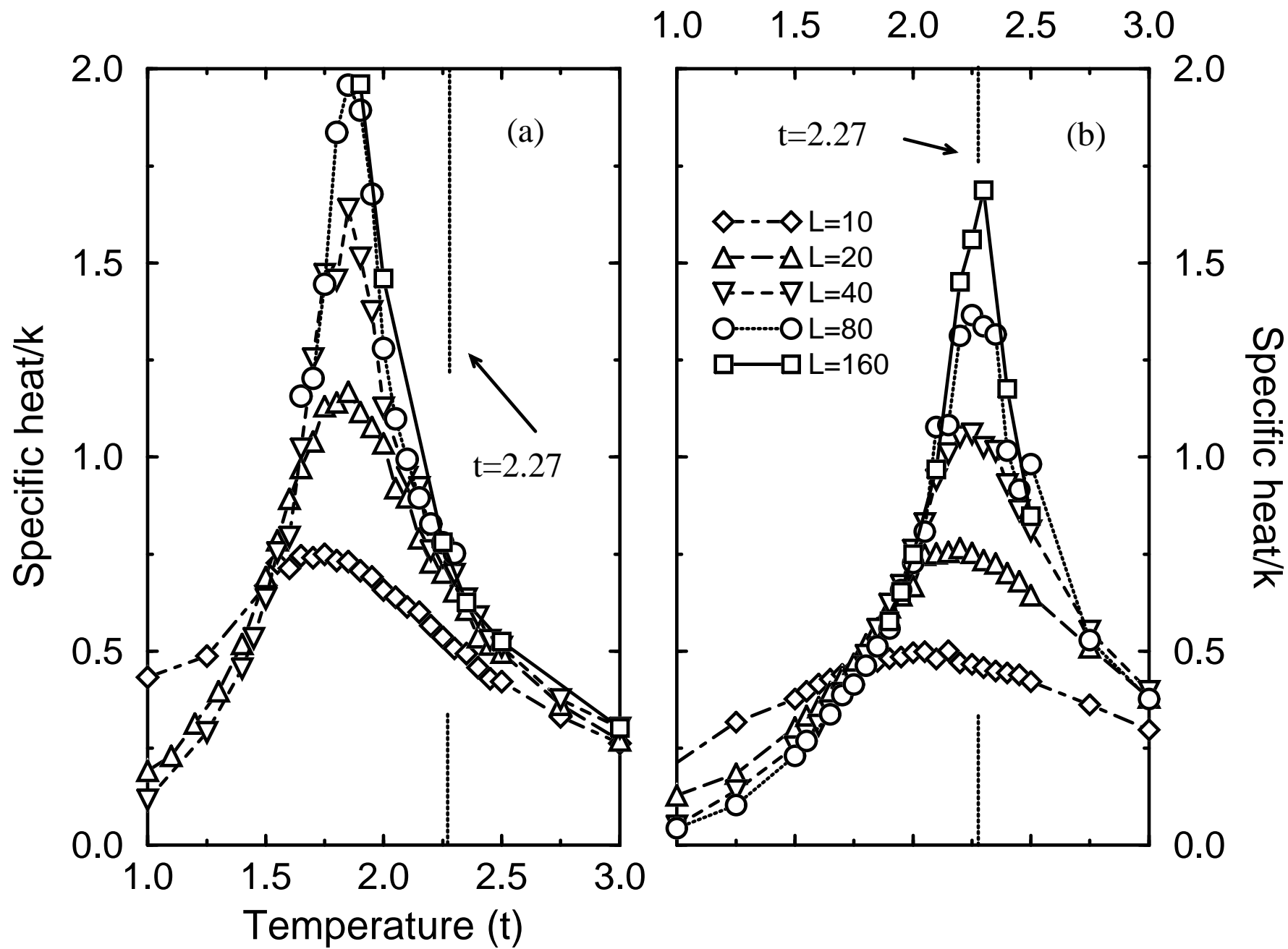
Figure 3

Figure 4

Figure 5

Figure 6

Figure 7